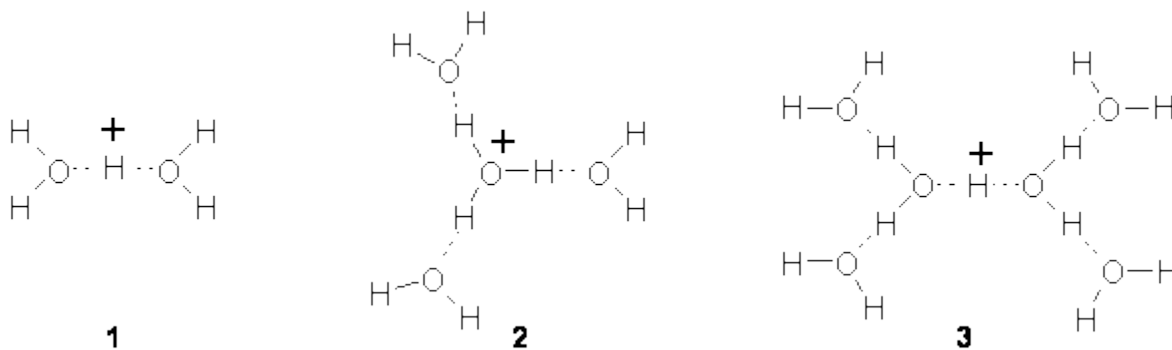


STRUCTURE OF THE HYDRATED PROTON

Stoyanov and Reed¹ have reported the IR spectrum of strong acid in water, trying to identify the true nature of the hydrated proton. In other words, what is n in the formula $\text{H}(\text{H}_2\text{O})_n^+$? The key to addressing this problem is to carefully measure the IR spectrum and then remove the signals due to (a) water associated with (or perturbed by) the anion and (b) bulk water. Simply subtracting out bulk water overcorrects because some waters are associated with the proton. By properly scaling the bulk water peak, they identify n as six. Deconvolution of the spectrum of $\text{H}(\text{H}_2\text{O})_6^+$ gives peaks at 3134 ± 12 , 2816 ± 40 , 1746 ± 11 , 1202 ± 4 and $654 \pm 12 \text{ cm}^{-1}$.

They suggest that the hydrated proton has structure **3**, which is distinguished from previous proposals of $\text{H}(\text{H}_2\text{O})_4^+$ **2** and $\text{H}(\text{H}_2\text{O})_2^+$ **1**.



Somewhat surprising is that these authors did not compute the structures of these ions and their IR spectrum. So just to motivate further work I have computed the spectrum of the three ions at PBE1PBE/6-311++G(2df,p)//PBE1PBE/6-31+G(d,p) (Figure 1) and their uncorrected IR frequencies within the range 500-3000 cm^{-1} (and intensities greater than 50) are listed in Table 1.

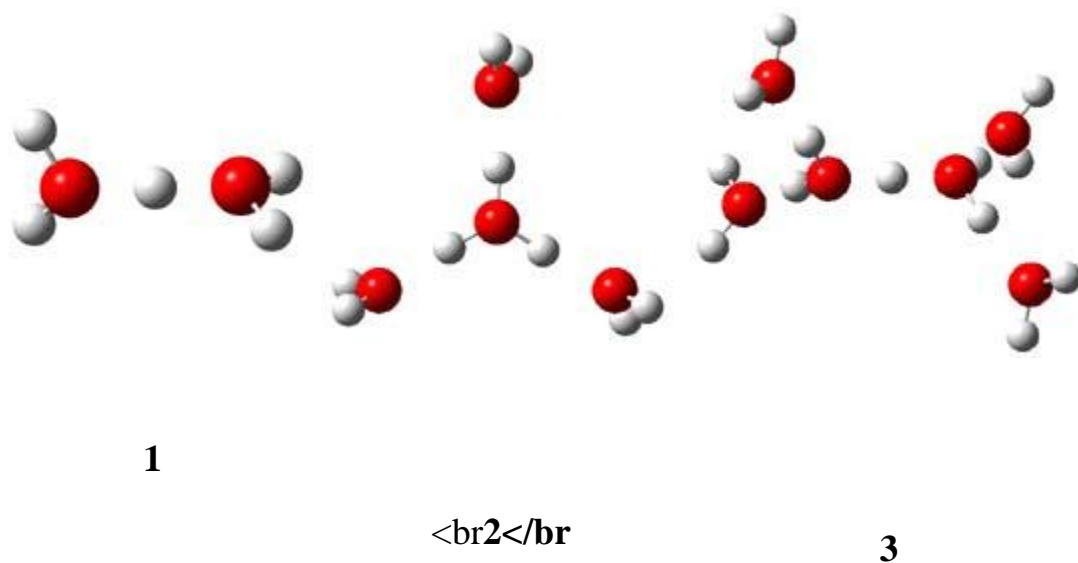


Figure 1. PBE1PBE/6-31+G(d,p) structures of **1** and **3** and PBE1PBE/6-311++G(2df,p) of **2**.

Table 1. Computed frequencies (cm^{-1}) and intensities of **1-3**.

<u>1</u>		<u>2</u>		<u>3</u>	
<u>v</u>	<u>I</u>	<u>v</u>	<u>I</u>	<u>v</u>	<u>I</u>
1082	2377	1024	66	857	709
1490	302	1199	313	887	63
1535	122	1634	75	938	137
1786	1554	2864	3180	1091	3310
		2994	151	1465	237
				1620	117
				1640	80
				1643	154
				1647	44
				1780	1002

The comparison between experiment and computation leaves something to be desired and more careful computation is clearly warranted. In addition, these types of complexes are likely to be dynamic, and so multiple different configurations and conformations will need to be sampled. So, again to promote contributions to this problem, I offer three other configurations of $\text{H}(\text{H}_2\text{O})_6^+$, shown in Figure 2. Their computed IR frequencies are listed in Table 2. Any additional interested takers?



3b

-0.48 (0.60)

3c

3.41 (4.80)

3d

-1.33 (1.33)

Figure 2. PBE1PBE/6-31+G(d,p) structures of **3b-3d** along with their relative (to **3**) electronic energy (kcal mol⁻¹ and electronic energy with ZPE (in parenthesis).

Table 2. Computed frequencies and intensities of **3b-3d**.

<u>3b</u>		<u>3c</u>		<u>3d</u>	
<u>ν</u>	<u>I</u>	<u>ν</u>	<u>I</u>	<u>ν</u>	<u>I</u>
546	52	503	154	603	89
834	136	584	307	731	166
845	153	605	53	800	162

959 86 618 148 928 101
1123 60 693 117 952 92
1258 232 882 171 1283 283
1632 90 1247 199 1637 224
1638 69 1582 582 1818 170
2550 4347 1645 115 2684 1877
2703 1791 1706 238 2841 2808
2013 3235
2267 2100

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